

PYROLYSIS OF COTTON SEED AND CHARACTERIZATION OF THE LIQUID PRODUCT

A Thesis submitted in partial fulfillment of the

requirements for the Degree of

BACHELOR OF TECHNOLOGY

in

CHEMICAL ENGINEERING

Submitted by

Suprabhat Seal

(Roll No. 109CH0093)

Supervisor:

Dr. R.K Singh



DEPARTMENT OF CHEMICAL ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

2013

CERTIFICATE

This is to certify that the work in this report entitled **“Pyrolysis of Cotton Seed and characterization of the liquid product”** submitted by **Suprabhat Seal (Roll Number 109CH0093)** in partial fulfillment of the requirements of the prescribed curriculum for Bachelor of Technology in Chemical Engineering Session 2009-2013 in the Department of Chemical Engineering, National Institute of Technology Rourkela, is an authentic work carried out by him under my supervision and guidance. To the best of my knowledge the matter embodied in the report is his bona fide work

Prof. R.K. Singh

Head of the Department

Date :

Department of Chemical Engineering

National Institute of Technology, Rourkela

Odisha 769008

ACKNOWLEDGEMENT

I take this opportunity to express my gratitude to all those who motivated, encouraged and helped me in this project work.

I wish to thank Prof. R.K.Singh my supervisor, for his constant support and guidance throughout the course of the project. I also wish to thank Prof. R.K. Singh, Head of Department, & Prof. H.M. Jena for providing me an opportunity to carry out the work and express my indebtedness towards the Department of Chemical Engineering, NIT Rourkela, for supporting me in successfully completing the project.

I also wish to thank Mr. Sachin Kumar (PhD Student), Ms. Debalakshmi Pradhan(PhD student), Mr. Tanmaya Rout (M. Tech Student) and Mr. Siba Sankar Sethi (B.Tech student) for their support and guidance during the project. Special thanks to other members of the department for being so supportive and helpful in every possible way.

(SUPRABHAT SEAL)

Roll Number : 109CH0093

ABSTRACT

There are several procedures to extract the energy out of biomass. One of them, that has assumed particular importance is pyrolysis. In this work, cotton seed has been chosen as the material of interest and serves as biomass. These cotton seed samples have been subjected to pyrolysis and the effect of pyrolysis temperature on the yield of liquid product, char and volatile were studied. The main objective of this work was to determine the possibility of finding a product that may serve as a fuel or may be used as a valuable product. Pyrolysis experiments were carried out in the temperature range of 350⁰C to 600⁰C. The liquid product was characterized using methods like FTIR and GCMS and its physical properties were determined using standard procedure prescribed in literature.

CONTENTS

1 Introduction.....	1
2 Literature review.....	4
2.1 Biomass	
2.2 Constituents of biomass	
2.3 Biomass conversion	
2.3.1 Physical Process of conversion	
2.3.2 Bio-chemical Process of conversion	
2.3.2.1 Alcoholic Fermentation	
2.3.2.2 Anaerobic digestion	
2.3.3 Thermo-chemical process of conversion	
2.3.3.1 Gasification	
2.3.3.2 Pyrolysis	
2.3.3.2.a Fast pyrolysis	
2.3.3.2.b Slow pyrolysis	
3. Experimental Section.....	13
3.1 Raw material	
3.2 Characterization of the raw material	
3.2.1 Proximate Analysis	
3.2.2 Ultimate Analysis	
3.2.3 Thermo-gravimetric Analysis	
3.3 Experimental set up and procedure	
3.4 Sample pyrolysis run	
3.5 Physical characterization of liquid product	
3.6 Chemical Characterization of liquid product	
3.6.1 FTIR	
3.6.2 GC-MS Analysis	
3.6.3 Ultimate Analysis of liquid product	
4. Result and Discussion.....	20
4.1 Characterization of raw material	
4.1.1 Proximate Analysis	
4.1.2 Ultimate Analysis	
4.1.3 Thermo gravimetric Analysis	
4.2 Variation of product yield with temperature of pyrolysis	
4.3 Characterization of Liquid Product	
4.3.1 Physical Characterization	
4.3.2 Chemical Characterization	
4.3.2.a GC-MS	
4.3.2.b FTIR Analysis	
4.3.2.c Ultimate Analysis of Liquid product	
5 Conclusion.....	30

LIST OF FIGURES

<u>Figure No.</u>	<u>Title</u>
2.1	Structure of cellulose
2.2	Structure of hemicellulose
2.3	Structure of lignin
3.1	Reactor-Furnace arrangement
4.1	TGA of Cotton seed
4.2	Product yield with variation of temperature
4.3	IR Spectra of the liquid product

LIST OF TABLES

<u>Table No.</u>	<u>Title</u>
3.1	Standard methods for physical property determination
4.1	Proximate Analysis of Cotton seed
4.2	Ultimate Analysis of Cotton seed
4.3	Variation of product yield with temperature
4.4	Physical properties of the obtained liquid product
4.5	GC-MS of the liquid product
4.6	FTIR compound and frequency table

NOMENCLATURE

GC-MS	Gas chromatography mass spectroscopy
FTIR	Fourier transform infra red spectroscopy
BTL	Biomass to liquid
TGA	Thermogravimetric analysis
GCV	Gross calorific value

Chapter 1

INTRODUCTION

1. INTRODUCTION

The three basic requirements for survival of man are food, shelter and clothing. However, with rapid industrialization, all these three requirements need energy for their synthesis, production or manufacture. It will not be a mistake to say that man has only one requirement and that is 'energy'. Today energy is the basic need for any kind of development. And a country's power is judged by its self-sufficiency and independence in terms of energy production and its utilization. Talking about energy, the most obvious thing that comes to our mind is the energy derived from fossil fuel. As a matter of fact, 19th century would not have seen such rapid pace of industrialization and urbanization, had it not been for the discovery of these indispensable and invaluable sources of energy. The three major sources of energy are Crude oil, Coal and Natural gas. While crude oil has an animal origin and has been formed from the remains of dead animals buried under the earth crust thousands of years ago, coal and natural gas have a vegetable matter origin and have been formed by a process similar to crude oil where remains of dead plants were subjected to the extreme conditions of the earth's crust for thousands of years.

As is suggestive from the origin of these sources, they are all non-renewable and once used, they can never be reused. This non-renewability of the fossil fuel introduces us to the problem of depletion of these sources. And owing to the rapid population increase and urbanization, the demand for energy has reached a level where we find ourselves at the brink of an acute energy crisis. Fossil fuel, though a very good source of energy, are on the verge of extinction. It is estimated that by 2100, most of our oil reserves will be exhausted. This perpetually decreasing trend of the fossil fuel reserves, have pushed the oil prices to very high level. There will be a point when buying petroleum will not be every man's cup of tea and only the rich will be able to afford these resources. Besides this, environmental concern is a big issue these days. The end products of combustion of these fossil derived fuels are causing a major irreparable damage to our environment. Mostly it releases CO₂, which is a green house gas and causes global warming. Most of the countries are adopting a zero tolerance approach towards these emissions and it has become the need of the hour to produce fuel that is eco-friendly. The fast depleting fossil reserves, ever-increasing price of these fuels and adverse environmental impact of these fuels have made it extremely important to look for alternative sources of energy, source that is renewable and is economically feasible besides being environment friendly.

Currently available reserves of these fossil fuels may serve us comfortably for another century but once that is depleted, there is no means we can get it back. It is thus immensely important at this point to look for alternative methods of production or sources of energy. Failure to do this will send us back to pre-industrialization era.

In this context, scientists and researchers have come up with several alternatives which are renewable sources of energy. Some of which are wind energy, solar energy, hydel energy, geothermal energy, energy derived from biomass, etc. These sources though serve as an alternative, have not been exploited to the extent where they have proved themselves to be economically viable. And most, except the energy derived from biomass, have been used with very little use on a commercial scale.

Biomass has been found to be a source of a variety of useful chemicals and fuels. Thermal pyrolysis of biomass produces solid, liquid and gaseous products. The yield of liquid product can be as high as 75% by weight [1]. The liquid product contains various organic and inorganic compounds including aldehydes, ketones, hydrocarbons, organic acids, etc. With suitable methods of separation, the liquid product can be separated into various fractions some which may serve as fuel. Others can be used as important chemicals or as a starting material for other important products. Biodiesel is one of the fuels produced by the pyrolysis of biomass. India has already harnessed this technology to some extent. The first biodiesel plant in India was setup in the year 2006 at Kakinada, a city of Andhra Pradesh. This plant uses Belgian technology to produce about 30 million gallons of bio diesel per year from Jatropha seeds. This fuel is cheaper than the conventional diesel and had been used as a substitute to conventional diesel. All in all, there are biodiesel plants in more than 9 states of India. Indian Railways is the first consumer of biodiesel in the Public Sector. Generally the fuel used by Indian railways is a blend of biodiesel and conventional diesel in various proportions and is efficiently used in the diesel engines of the railway locomotives.

Chapter 2

LITERATURE REVIEW

2. LITERATURE REVIEW

2.1 BIOMASS

Biomass refers to any organic materials that are derived from plants or animals. In general it is difficult to find out the actual definition. Biomass is non-fossilized and biodegradable organic material originating from plants, animals and micro-organisms. This includes the products, byproducts, residues and wastes from agriculture, forestry, industrial and municipal wastes. Biomass also includes gases and liquids recovered from the decomposition of non fossilized and biodegradable organic materials. As a sustainable and renewable energy resource, biomass is constantly being formed by the interaction of CO₂, air, water, soil, and sunlight with plants and animals. When an organism dies, microorganisms break down into elementary constituent parts like H₂O, CO₂, and its potential energy. Because plants use the same the carbon dioxide at the time of photosynthesis, the amount of CO₂ does not increase in the earth. It is thus called greenhouse gas neutral or GHG neutral. It does not include organic materials that converted to coal or petroleum over many millions of years by geological processes. Biomass comes from botanical (plant species) or biological (animal waste or carcass) sources, or from a combination of these.

2.2 CONSTITUENT OF BIOMASS

The major constituents of biomass are cellulose, hemicelluloses and lignin. [2]

Cellulose

The primary organic component of the cell wall of the biomass is cellulose. It is represented by generic formula (C₆H₁₀O₅)_n. Cellulose is of a crystalline, strong structure that is resistant to hydrolysis and a long chain polymer with a high degree of polymerization (~10,000) and a large molecular weight (~500,000). Cellulose is primarily composed of d-glucose, which is made of six carbons (fig. 2.1). Cellulose is highly insoluble and, though a carbohydrate is not digestible by humans. It is a dominant component of wood, making up about 40 to 44% by dry weight. Its amount varies from 90% (by weight) in cotton to 33% for most other plants.

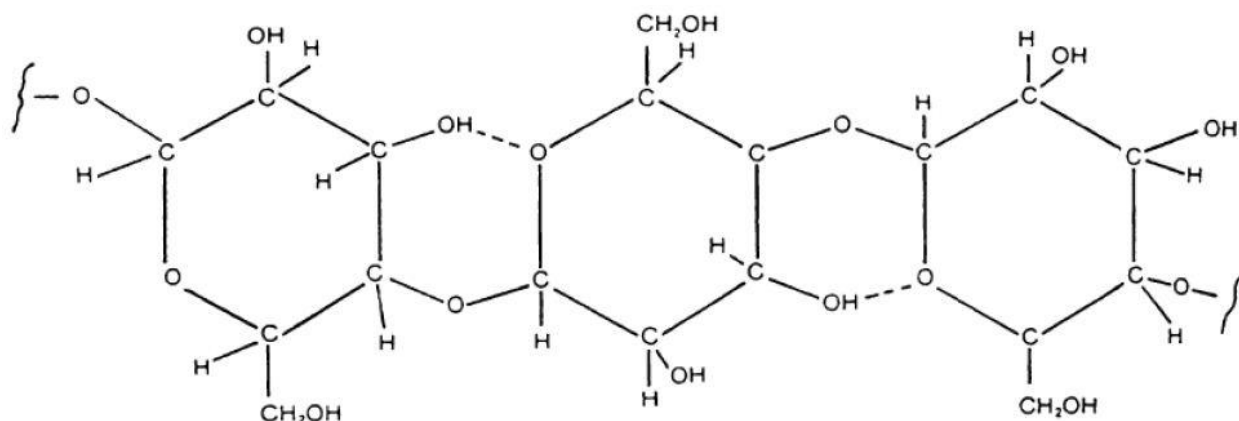


Figure 2.1 *Structure of cellulose*

Hemicelluloses

The constituent of the cell wall of the plant is hemicelluloses and represented by the generic formula $(\text{C}_5\text{H}_8\text{O}_4)_n$. It is a group of carbohydrates with a branched chain structure and a lower degree of polymerization (~ 100 – 200) [Fig.2.2 Shows](#) the molecular arrangement of a typical hemicelluloses molecule, it constitutes about 20 to 30% of the dry weight of most wood. The composition and structure of hemicelluloses varies from biomass to biomass. Most of the hemicelluloses contain some simple sugar residues like D-xylose (the most common), D-glucose, D-galactose, D-arabinose, D-glucuronic acid, and D-mannose. These typically contain 50 to 200 units in their branched structures. It is soluble in weak alkaline solutions and is easily hydrolyzed by dilute acid or base. The presence of hemicelluloses yields more gases and less tar than cellulose at the time of decomposition.

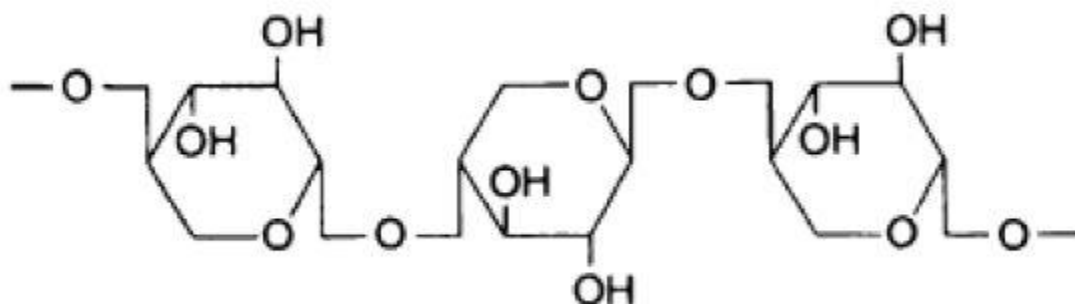


Figure 2.2 *Structure of hemicellulose*

Lignin

The third important constituent of woody biomass is lignin, which is complex in nature, highly branched polymer of phenyl propane and is an integral part of the secondary cell walls of plants. It is primarily a three dimensional polymer of 4-propenyl phenol, 4-propenyl-2-methoxy phenol, and 4-propenyl-2,5-dimethoxy phenol. It is one of the most abundant organic polymers on Earth (exceeded only by cellulose). Lignin is the cementing agent for cellulose fibers holding adjacent cells together. The dominant monomer units in the polymers are benzene rings. Fig. shows some structure of lignin, which is composed primarily of lignin, glues together adjacent cells. Lignin is highly insoluble, even in sulphuric acid. A typical hardwood contains about 18 to 25%, while softwood contains 25 to 35% by dry weight.

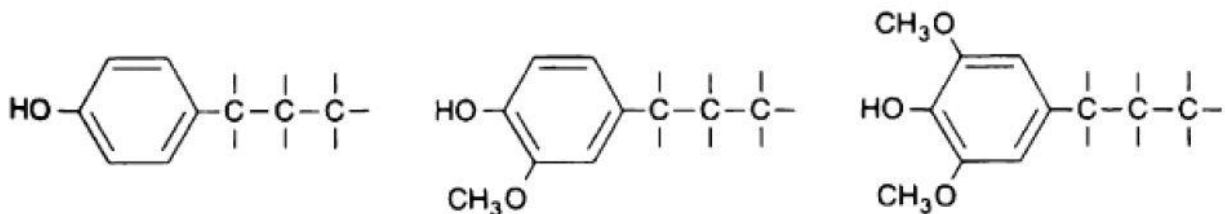


Figure 2.3 *Structure of lignin*

2.3 BIOMASS CONVERSION

Biomass can be converted into useful by three main processes:-

- Physical Process
- Biochemical Process
- Thermo-chemical Process

2.3.1 PHYSICAL PROCESS OF CONVERSION

The physical process of conversion is generally applicable to Oil Seeds. In this process, oil is extracted from the oil bearing seeds and the extracted oil is then subjected to esterification with alcohol to reduce the viscosity and improve the quality of the biofuel.

2.3.2 BIOCHEMICAL PROCESS OF CONVERSION

This process is mostly used for semi-solid or liquid biomass having high percentage of water. It mainly depends on the action of microorganism on wet biomass in presence or absence of oxygen. Biochemical process of conversion can either be alcoholic fermentation or anaerobic digestion.

2.3.2.1 ALCOHOLIC FERMENTATION

Fermentation is applied in the production of alcoholic wines from sugar crops and starch crops. Ethanol can be produced from biomass material in the presence of organisms (e.g. yeast) that gives a high quality fuel for storage and transport. Biochemical conversion of wastes is more difficult for the fermentative degradation and need first to be broken down by acidic or enzymatic hydrolysis because of the presence of longer-chain polysaccharides. Product ethanol after distillation purification can be used as a supplement or substitute for petrol. Biomass materials for alcoholic fermentation are generally agricultural production/processing residues. Molasses which is a by-product of sugar-manufacturing process has been industrially converted for the production of ethanol.

2.3.2.2 ANAEROBIC DIGESTION

Anaerobic digestion is the degradation of organic wastes through microbial actions in the absence of oxygen to produce reducing gases (biogas) which mainly composed of methane, carbon dioxide and contains trace components which is hydrogen sulfide, acids and thiols. One example is the landfill gas (LFG) buried in sanitary landfill sites. LFG, which consists of up to 50% methane, can be purified and then burned in engines or turbines to produce heat and electricity. Biogas is generally produced from animal manure in an airtight container (digester). Because of high heating Value (5400–6000 kcal/Nm³) of biogas, the biogas can be directly used in burners, also can be used as gas fuel in internal combustion engines to generate electricity, or can be upgraded to natural gas quality by the removal of carbon dioxide and hydrogen sulfide.

2.3.3 THERMO-CHEMICAL PROCESS OF CONVERSION

In thermo-chemical conversion, biomass is converted into gas & liquid intermediates that can be used for fuels and chemical synthesis. The term Biomass to Liquid (BtL) is applied to synthetic fuels produced from biomass via thermo-chemical route. The objective is to produce fuel components that are similar to those of current fossil-derived petrol (gasoline) and diesel fuels and hence can be used in existing fuel distribution systems and with standard engines. They are also known as syn-fuels.

The two main technologies under thermo chemical conversion are listed below

- Gasification
- Pyrolysis

The intermediate products include clean syngas ($\text{CO} + \text{H}_2$), bio-oil (pyrolysis or hydrothermal product), and gases rich in methane or hydrogen. These intermediates can further be synthesized to gasoline, diesel, alcohols, ethers, synthetic natural gas etc. and also high purity hydrogen, which can be used as fuels in electric power generation.

2.3.3.1 GASIFICATION

When biomass is heated with only about one-third the oxygen needed for efficient combustion, it gasifies to a mixture of carbon monoxide and hydrogen. This gaseous mixture is called synthesis gas or syn-gas.

2.3.3.2 PYROLYSIS

Pyrolysis is mainly concerned with thermo-chemical process for conversion of biomass. It involves heating the biomass at high temperature in absence of air which produces gaseous products and later can be condensed to give liquid fuels consisting of pyrolytic oil or bio-oil and oily water (mixture of water and certain hydrocarbons). In a good operational condition almost 70-80% of gaseous products are converted to liquid fuels which later can be modified according to its use. This process is a very popular process which makes a good quantity of liquid fuel from biomass, which is very similar to commercial transportation fuels and can be upgraded or modified to replace transportation fuel[10]. It also provides some amount of gaseous and solid products which have higher market value as they can also be used as a source of energy. Longer vapor residence times and lower process temperatures favor the production of charcoal. Longer residence times and High temperatures increase biomass conversion to gas, and short vapor residence time and moderate temperatures are optimum for producing liquids. Mostly three products are always produced, but the composition can change over a wide range by adjustment of the process parameters. Biomass decomposes rapidly to produce mostly vapors and aerosols and some charcoal and gas. When cooling and condensation takes place, a dark brown homogenous mobile liquid is formed which has a heating value about half that of conventional fuel oil. With most biomass feeds low in ash a high yield of liquid is obtained. The features of a pyrolysis process for producing liquids are [3][4] :

1. Very high heating rates and heat transfer rates at the biomass particle reaction interface favors a finely ground biomass feed of typically less than 3 mm as biomass generally has a low thermal conductivity.

2. Controlled pyrolysis reaction temperature of around 500 °C to maximize the liquid yield for most biomass.
3. Vapor residence times of typically less than 2 s to minimize secondary reactions.
4. Product char is removed to minimize cracking of vapors.
5. Pyrolysis vapors are rapidly cooled to give the bio-oil product.

Pyrolysis for liquids takes less time, phase transition phenomena and heat and mass transfer processes, as well as chemical reaction kinetics, play important roles. The reacting biomass particles are brought to the optimum process temperature also to minimize their exposure to the lower temperatures that favor formation of charcoal. Small particles can be used, for example in the fluidized bed processes. Heat is transferred very fast only to the particle surface that contacts the heat source which is used in ablative processes. Main product which is bio-oil, is obtained in yields of up to 75 wt. % on a dry-feed basis, together with by-product char and gas which is used within the process to provide the process heat requirements so that there are no waste streams other than flue gas and ash. Liquid product depends on hot vapor residence time, biomass ash content, biomass type, temperature, and hot vapor residence time and char separation[11]. In pyrolysis process the material is dried to less than 10% water in order to minimize the water in the product liquid oil, the feed is grinded to give sufficiently small particles to ensure rapid, fast and efficient separation of solids (char), and rapid quenching and collection of the liquid product (often referred to as bio-oil). Any form of biomass can be considered for fast pyrolysis. Maximum work has been done on wood and more than 100 different biomass types already been tested by many laboratories, olive pits and nut shells to energy crops such as miscanthus and sorghum, from agricultural wastes such as straw, forestry wastes such as bark and solid wastes such as sewage sludge and leather wastes.

A commercial process constitutes three main stages from feed to delivery of one or more useful products:

1. Feed, storage, handling, preparation and pretreatment;
2. Fast pyrolysis to a more usable form of energy in liquid form which is known as bio oil;
3. Liquid product is converted by refining, processing and can be used as electricity, heat, and chemicals.

The advantage of pyrolysis is because it can convert biomass directly into liquid, gaseous products and solid by thermal decomposition of biomass in the absence of oxygen [5]. Pyrolysis is of two types. They are

- a. Fast Pyrolysis
- b. Slow Pyrolysis

2.3.3.2.a FAST PYROLYSIS [12]

In fast pyrolysis process the feed stock is rapidly heated (high rate of heating) in absence of oxygen at high temperature. During the decomposition, biomass generates vapors, aerosols, and some charcoal-like char. After cooling and condensation of the vapors and aerosols, a dark brown mobile liquid is formed that has a heating value that is about half that of conventional fuel oil. Fast pyrolysis is a more advanced process that can be carefully controlled to give high yields of desired liquid products. Fast pyrolysis process produces 60-75 wt % of liquid biooil, 15-25 wt % of solid char, and 10-20 wt % of non-condensable gases, depending on the feedstock used. No waste is generated, because the bio-oil and solid char can each be used as a fuel and the gas can be recycled back into the process. Fast pyrolysis of rape seed was carried out by Onay et al. in a well-swept fixed bed reactor and reported that the maximum yield is 68% at pyrolysis temperature of 550⁰ C with particle size 0.6–0.85mm, heating rate of 300°C/min and N₂ flow rate of 100cm³/min. Fast pyrolysis of rape seed was also done by Kockar et al. and investigated effect of temperature, heating rate, particle size, and sweep gas flow on the product yield and concluded that, the yield of char decreases to 14.5% from 27% with increasing in temperature and maximum 73% yield of oil at a temperature of 550–600⁰ C, particle size of +0.6–1.25 mm, and sweep gas flow rate of 100 cm³/min. Fixed-bed fast pyrolysis experiments have been conducted on cottonseed cake by Nurgu et al. to determine the effects of pyrolysis temperature, heating rate and sweep gas flow rate on pyrolysis yields of the product oil and concluded that the maximum oil yield of 34.8% final temperature of 550°C with a heating rate of 700°C/min and nitrogen flow rate of 100cm³/ min.

2.3.3.2.b SLOW PYROLYSIS

Slow pyrolysis is also known as conventional pyrolysis. When pyrolysis is carried out at slow heating rate (3-7K/min), it is known as slow pyrolysis. Several literatures reveal that in case of

slow pyrolysis, the yield of oil is less and char yield is more. Conventional pyrolysis involves all three types of pyrolysis product (gas, liquid, and char). As such, it heats the biomass at a moderate rate to a moderate temperature ($\sim 600^\circ\text{C}$). The product residence time is on the order of minutes. The slow pyrolysis of pomegranate seeds was carried out by Suat Uçar et al. at 400, 500, 600 and 800°C to know the effect of temperature on the product distribution. The maximum liquid yields were obtained at the temperatures of 500 and 600°C and the biochars produced from pomegranate seeds having carbon rich fuels with high bulk densities and calorific values. Beis et al.[15] slowly pyrolysed Safflower seeds in Fixed-bed pyrolyzer to determine particularly the effects of pyrolysis temperature, heating rate, particle size and sweep gas flow rate on the pyrolytic product yields and their chemical compositions and obtained the maximum oil yield of 44% at temperature of 500°C , particle size range of $+0.425\text{--}1.25\text{ mm}$, with heating rate of $5^\circ\text{C}/\text{min}$ and sweep gas (N_2) flow rate of $100\text{ cm}^3/\text{min}$. [6][13]. Safflower (*Charthamus tinctorius* L.) seed press cake was pyrolyzed in a fixed-bed reactor from temperature $400\text{--}600^\circ\text{C}$ at different heating rate (10, 30, $50^\circ\text{C}/\text{min}$) under the sweep gas of N_2 with a flow rate of $100\text{ cm}^3/\text{min}$. to investigate the effects of pyrolysis temperature, heating rate and sweep gas flow rates on the yields of the products by Sensoz et al. and obtained the maximum yield of bio-oil 36% by weight at 500°C with a heating rate of $50^\circ\text{C}/\text{min}$ under the sweep gas of N_2 with a flow rate of $100\text{ cm}^3/\text{min}$. due to the decrease in mass transfer limitations. Sensoz et al. studied the Pyrolysis behavior of cotton-seed cake under clinoptilolite catalyst at different conditions and investigated the effect of pyrolysis temperature, catalyst and sweeping gas flow rate and concluded that maximum 30.84% of liquid yield at temperature of 550°C , sweeping gas flow rate of $100\text{ cm}^3/\text{min}$ in the presence of clinoptilolite catalyst (20% based on raw material).[7][16][17] Rapeseed cake was pyrolyzed by Filiz Karaosmanogi et al. in a fixed bed stainless steel reactor from temperature $450\text{--}850^\circ\text{C}$ under static atmosphere at rates of $15^\circ\text{C}/\text{min}$ and $25^\circ\text{C}/\text{min}$ towards understanding the influence of heating rate and pyrolysis temperature on product yield. The maximum yield was obtained at 650°C at a heating rate of $15^\circ\text{C}/\text{min}$. Pyrolysis experiments on soybean cake was carried out by E. Putun et al.[8][9][14] in a fixed-bed reactor under nitrogen and steam atmosphere and obtained the maximum yield of oil 33.78% at 550°C of particle size $0.850 > D_p < 1.250\text{ mm}$ when sweeping gas (N_2) flow rate was $200\text{ cm}^3/\text{min}$ and the oil yield increased to 42.79% with a steam velocity of 1.3 cm/s .

Chapter 3

EXPERIMENTAL METHODS

3. EXPERIMENTAL METHODS

3.1 RAW MATERIAL

Cotton Seed has been used as the raw material for the pyrolysis experiments. These seeds were collected from local market in Rourkela. Before carrying out pyrolysis experiments, the seeds were crushed to fine powder and then dried in an oven at about 105⁰C to remove all the free moisture.

3.2 CHARACTERIZATION OF RAW MATERIAL

3.2.1 PROXIMATE ANALYSIS

Proximate analysis estimates the % of moisture, volatile matter, ash and fixed carbon content in a sample. The procedure to estimate each of these quantities is as follows:

i. Determination of moisture content

One gram of air dried sample was taken in a crucible and kept in an electrically heated oven at a temperature of 105⁰C for one hour. After one hour the sample was taken out and cooled in desiccators. The percentage loss of weight gave the percentage of moisture in the sample.

Percentage of moisture content = loss in weight * 100/ wt. of sample taken

ii. Determination of volatile matter

The dried samples after moisture removal was then taken in a crucible and placed in an electrically heated furnace at a temperature of 925⁰C for seven minutes and then cooled in desiccators. The percentage of weight loss gave the volatile matter content.

Percentage of volatile matter = loss due to removal of volatile matter*100/ wt. of sample taken

iii. Determination of ash content

The remaining sample after determination of volatile matter was kept in furnace at a temperature of 725⁰C for one and half hour. The percentage of weight loss gave the ash content.

Percentage of ash = weight of ash left*100/ wt. of sample taken

iv. Determination of fixed carbon

Percentage of fixed carbon = 100- % of (moisture +volatile+ ash) content

3.2.2 ULTIMATE ANALYSIS

Ultimate analysis is used to determine the elemental composition of the sample. This includes determination of carbon, hydrogen, nitrogen, sulfur, oxygen contents of the material. For the specific applications, other chemical analyses can be employed. These include identifying the forms of sulfur present. Sulfur occurs in the form of sulfide minerals, sulfate minerals, or organically bound sulfur. Other specific cases the analyses may involve determining the trace elements present which influence the suitability of the material for a particular purpose. This may include methods for reducing environmental pollution and so forth. It was carried out using a CHNSO elemental analyzer (Variael CUBE Germany) which provides carbon, hydrogen, nitrogen, sulphur percentage composition. And when sum of these compositions is subtracted from 100, it gives oxygen percentage composition.

3.2.3 THERMO-GRAVIMETRIC ANALYSIS

Thermo gravimetric analysis or thermal gravimetric analysis is mainly considered as a type of testing on samples which determines changes in weight to a temperature program in a controlled atmosphere. It relies on a high degree of precision in two basic aspects which is weight and temperature. As most weight loss curves look more or less similar, the weight loss curve may require keen analysis before results may be interpreted. A derivative weight loss curve can identify the point where weight loss is most prominent. Interpretation is limited without further modifications of the overlapping peaks. For the determination of the composition and purity one must take the mass of the substance in the mixture by using thermal gravimetric analysis. Thermal gravimetric analysis is a process which involves heating a mixture to a high enough temperature so that one of the components decomposes into a gas that dissociates into the air. Thermo gravimetric analysis is a process which utilizes heat and stoichiometry ratios to determine the percent by mass ratio of a substance. If the compounds in the material remain known, then the percentage by mass is determined by taking the weight of what is left in the mixture and dividing it by the initial mass. After knowing the mass of the original mixture and the total mass of impurities liberating upon heating then the stoichiometric ratio can be used to calculate the percent mass of the substance in a sample. TGA is used in research and testing to determine characteristics of materials such as absorbed moisture content of materials, the level of Inorganic and organic components in materials, polymers, to determine degradation temperatures,

decomposition points of explosives, and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation.

The analyzer consists of a high-precision balance with a pan of platinum loaded with the sample. Pan resides in a furnace and is heated or cooled during the experiment. Different process using a quartz crystal microbalance is devised for measuring smaller samples on the order of a microgram versus milligram with conventional TGA. Sample is placed in a small electrically heated oven with a thermocouple for accurate measurement of the temperature. The atmosphere may be supplied with an inert gas to prevent oxidation or other undesired reactions. A computer is employed to control the instrument.

Pyrolysis is heating of a substance in absence of air at a particular temperature. Therefore, the temperature for effective pyrolysis of the oil seeds has to be determined. For this purpose, thermo-gravimetric analysis (TGA) of the sample seed was done using a DTG60 instrument. Around 10 ~ 11 milligrams of sample seed was taken and heated up to a final temperature of 600°C and a residence time of 1 minute at 600°C was allowed. TGA was performed at a heating rate of 20°C/Min and in a nitrogen atmosphere. Thermo-gravimetric weight loss curve was plotted against temperature. It provides a range of temperature in which maximum thermal degradation of oil seeds takes place.

3.3 EXPERIMENTAL SET-UP AND PROCEDURE

The experiments were conducted in a reactor-furnace system in which the furnace temperature was maintained constant using a PID controller. The outlet of reactor was attached to a condenser to condense the vapors coming out of it and was collected in a measuring cylinder at the outlet of the condenser. Cotton seed sample was filled in a reactor of 300 ml capacity and the reactor was kept in the furnace for heating at constant temperature.

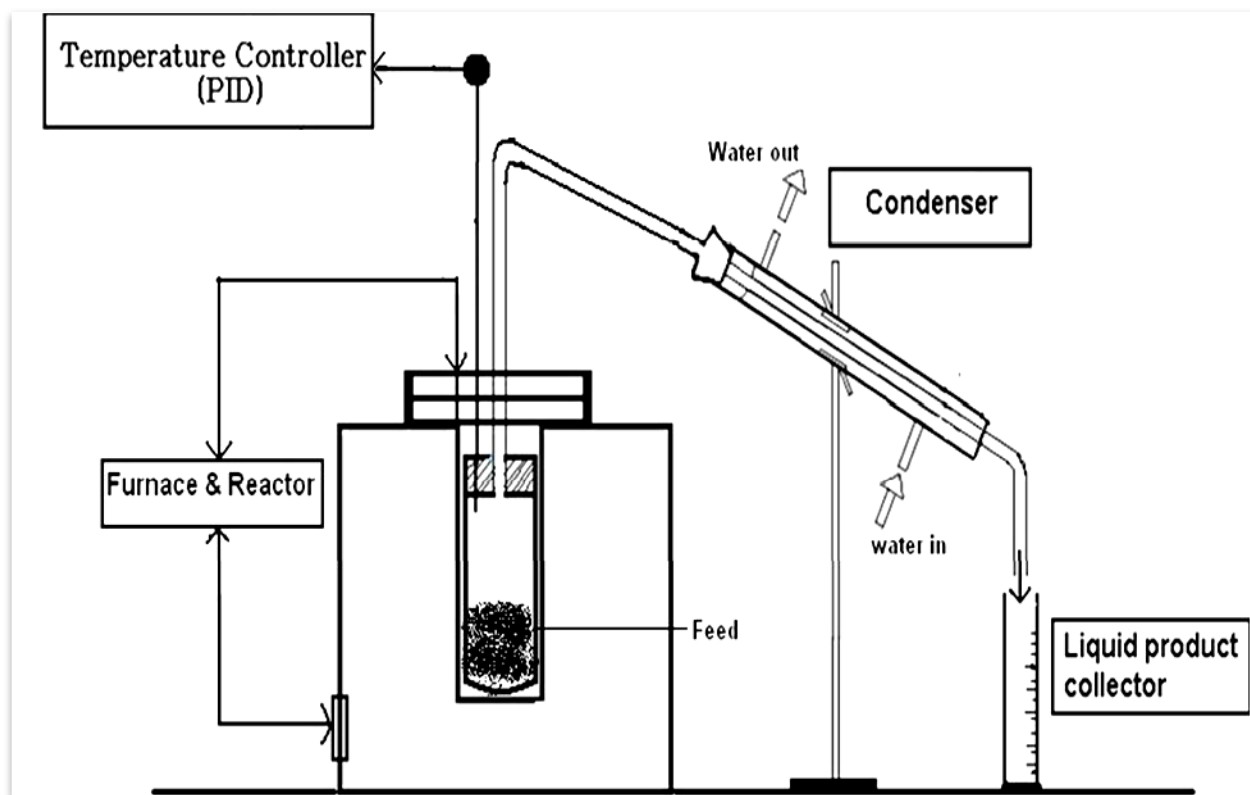


Fig. 3.1 *Reactor-Furnace arrangement*

The start of the reaction is indicated by vapors coming out of reactor through the provided outlet. These vapors get condensed in a condenser as shown in Fig 3.1. Water is used as cooling medium in the condenser and circulated via a pump. The condensed vapors are collected in a container as the liquid product whereas there is some amount of non-condensable gases which are simply left out. The liquid product collected contains oily water and bio-oil. Oily water is basically water with some dissolved hydrocarbons. Oily-water and bio-oil is further separated by difference in their density in a decanter.

3.4 SAMPLE PYROLYSIS RUN

Once the temperature range was established from the TGA curve then sample pyrolysis runs were done with 30 gm of seed in that range at intervals of 50 °C to determine the temperature at which maximum yield of liquid product is obtained. Various data like yield of char, and yield of liquid product were noted down during sample runs. Variation in yield of char, liquid product and gas (volatiles) with respect to temperature is studied.

3.5 PHYSICAL CHARACTERIZATION OF LIQUID PRODUCT

Physical properties such as density, specific gravity, viscosity, flash point, fire point, pour point, calorific value, sulfur content and cetane index of the liquid product were determined using the standard methods given in table 3.1

Table 3.1 Standard methods for physical property determination

Physical property	Methods
Density	ASTM D1298 – 99
Kinematic Viscosity	ASTM D445 – 11
Flash Point	ASTM D6450 - 05(2010)
Fire Point	ASTM D1310 - 01(2007)
Pour Point	ASTM D5853 - 09
Calorific Value	ASTM D5468 - 02(2007)
Cetane Index	ASTM D4737 - 10

3.6 CHEMICAL CHARACTERIZATION OF LIQUID PRODUCT

3.6.1 FTIR

Fourier Transform Infrared spectroscopy (FTIR) is an important analysis technique that detects various characteristic functional groups available in oil. Due to interaction of an infrared light with oil the chemical bond will stretch, contract, and absorb infrared radiation in a specific wave length range in the presence of the rest of molecules. Based on this, the principle functional groups present in the pyrolytic oil were identified. The FTIR spectra were collected generally in the range of 400-4000 cm^{-1} region with 8 cm^{-1} resolution.

Absorption in the infrared region makes changes in vibration and rotational status of the molecules. The absorption frequency depends greatly on the vibration frequency of the molecules. The absorption intensity depends on how the infrared photon energy can be transferred to the molecule. This depends on the change in the dipole moment that occurs as a result of molecular vibration. A molecule will absorb infrared light only if the absorption causes a change in the dipole moment. All compounds except for elemental diatomic gases such as N_2 , H_2 and O_2 , have infrared spectra and most components present in a flue gas is also analyzed by their characteristic infrared absorption. If only one species is analyzed, a species-specific instrument can also be used. Analysis is carried out in a narrow wavelength interval, where the species of interest has a characteristic absorption. Other components present in the sample also

absorb at the analytical wavelength, so the spectrometer should be calibrated for cross sensitivities. Quantification of several components absorbing in the mid infrared region (400-5000 cm^{-1}), either conventional dispersive infrared analysis or Fourier Transform Infrared (FTIR) spectroscopy can also be used. Compared to dispersive IR analysis, FTIR analysis is faster and has a better signal to noise ratio.

In a FTIR instrument, the monochromator and the slits are replaced by an interferometer of Michelson type. A beam of radiation is divided into two beams by means of a beam splitter. A path difference between the beams is also introduced whereupon it is allowed to recombine. In this way, interference between the beams is obtained. Intensity of the output beam from the interferometer is monitored as a function of path difference using an appropriate detector. In order to determine the functional groups present in the pyrolytic oil, Fourier Transform Infrared spectroscopy of the oil was analyzed in a Perkin-Elmer infrared spectrometer.

3.6.2 GC-MS ANALYSIS

GC-MS of the liquid product was performed using a GC-MS OP 2010[SHIMADZU] analyzer to determine the Chemical compounds present in the oil. Chromatography is specially used to separate mixtures of chemicals into individual components for identification. After isolation, the components can be evaluated individually. In almost all chromatography, separation generally occurs when the sample mixture is introduced or injected into a mobile phase. In case of liquid chromatography, the mobile phase is a solvent. In the gas chromatography (GC), the mobile phase is an inert gas for example helium. Mobile phase carries the sample mixture through what is referred as stationary phase. The stationary phase is considered as a chemical that can also attract components in a sample mixture. This tube is called as a column. Columns can be glass or stainless steel of various dimensions. The mixture of compounds in the mobile phase interacts with the stationary phase. Each and every compound in a mixture interacts at a different rate. That interact the fastest will exit (elute from) the column first. Those that interact slowest will exit the column last. By observing the changing characteristics of the mobile phase and the stationary phase the different mixtures of chemicals can be separated. Further refinements to this separation process are also made by changing the temperature of the stationary phase or the pressure of the mobile phase. GC has a long, thin column containing a thin interior coating of a solid stationary phase (5% phenyl-, 95% dimethylsiloxane polymer). This 0.25 mm diameter

column is called as a capillary column. This particular column is used for semi volatile, non-polar organic compounds such as the PAHs we will look at. The capillary column is held in an oven that can be programmed to increase the temperature gradually (or in GC terms, ramped). As the temperature increases, that compounds which have low boiling points elute from the column sooner than those that have higher boiling points. There are actually two distinct temperature, separating forces and stationary phase interactions mentioned previously. After the compounds are separated, they just elute from the column and enter a detector. Detector is capable of creating an electronic signal whenever the presence of a compound is detected. Greater the concentration in the sample the bigger the signal becomes. The signal is then processed by the computer. Time from when the injection is made (time zero) to when elution occurs is referred to as the retention time (RT). While the instrument runs, the computer generally generates a graph from the signal. Each of the peaks in the chromatogram represents the signal created only when a compound elutes from the GC column into the detector. The x-axis shows the RT, and the y-axis shows the intensity (abundance) of the signal.

3.6.3 ULTIMATE ANALYSIS OF LIQUID PRODUCT

Ultimate analysis of the liquid product was carried out to estimate the percentage of carbon, hydrogen, nitrogen, sulphur and oxygen content. It was carried out using a CHNSO elemental analyzer (Variael CUBE Germany) which provides carbon, hydrogen, nitrogen, sulphur percentage composition. And when sum of theses compositions is subtracted from 100, it gives oxygen percentage composition.

Chapter 4

RESULT AND DISCUSSION

4. RESULT AND DISCUSSION

4.1 CHARACTERIZATION OF RAW MATERIAL

4.1.1 PROXIMATE ANALYSIS

Table 4.1 shows the results for the proximate analysis of the cotton seed sample.

Table 4.1 Proximate Analysis of Cotton seed

Proximate Analysis of Cotton Seed	
% Moisture	10.05
% Volatile Matter	67.95
% Ash content	6
% Fixed Carbon	16

4.1.2 ULTIMATE ANALYSIS

Table 4.2 shows the results for the ultimate analysis of the cotton seed sample

Table 4.2 Ultimate Analysis of Cotton seed

Ultimate Analysis of Cotton Seed	
% N	4.47
% C	53.10
% H	3.55
% S	1.54
% O	37.34

4.1.3 THERMO-GRAVIMETRIC ANALYSIS

Fig 4.1 shows the TGA curve for cotton seed. The curve is a plot of weight percent versus temperature. As is evident from the figure most of the loss in weight occurs in the temperature range of 250 to 580 °C. This establishes the temperature range for the pyrolysis experiment.

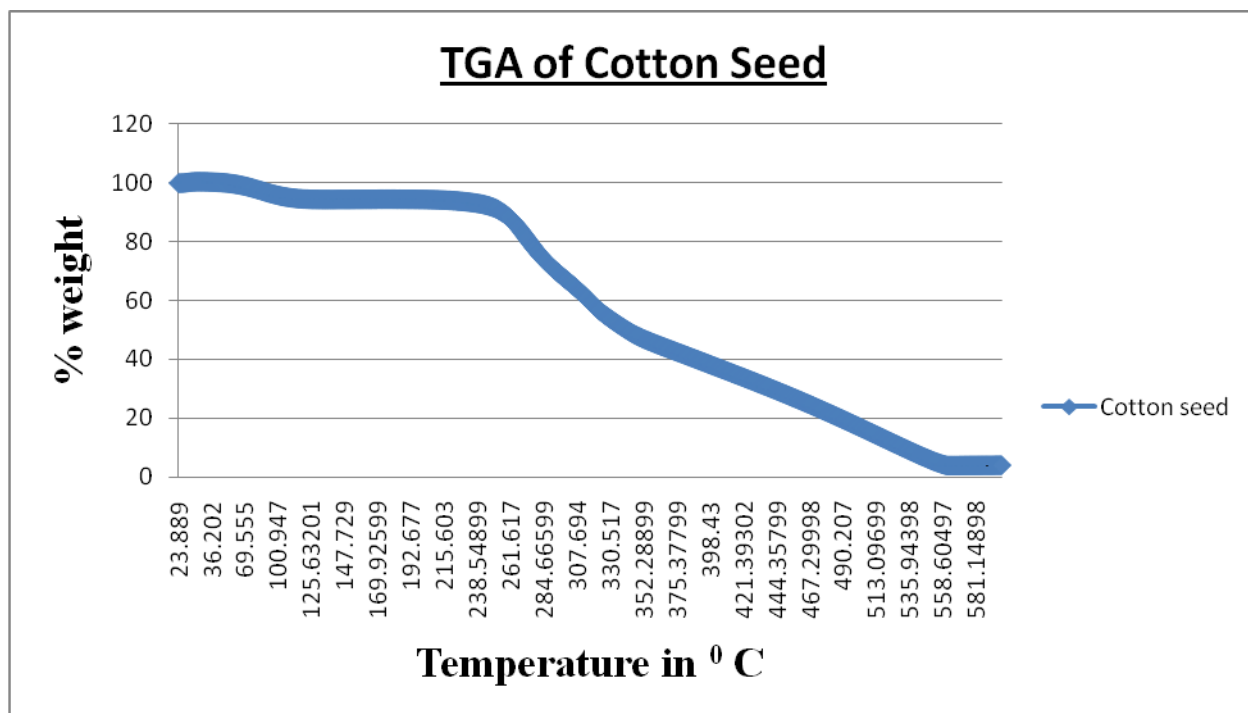


Fig. 4.1 TGA of cotton seed

4.2 VARIATION OF PRODUCT YEILD WITH TEMPRATURE OF PYROLYSIS

Table 4.4 shows the variation in yield of various liquid, solid and gaseous product with the variation of pyrolysis temperature. It can be seen from the table that with the increase in pyrolysis temperature, yield of liquid product increase until it reaches a maximum value. For cotton seed, this maximum is reached when the temperature reaches 550⁰C when the yield is about 58% by weight. Beyond the 550⁰C increase in temperature causes decrease in liquid yield. Similar but opposite trend is observed for the char yield. The temperature at which yield of liquid product is maximum, yield of char is minimum.

Figure 4.2 gives a graphical representation of the phenomenon mentioned above. The yield of volatile product was determined by method of difference and was not directly measured.

Table 4.3 Variation of product yield with temperature

Temp ($^{\circ}\text{C}$)	Liquid Vol.(mL)	Liquid wt. (gm)	Char Wt. (gm)	Wt % of Liquid	Wt% of Char	Wt% of Volatiles
375	11.5	10.95	13.19	36.5	43.97	19.54
425	13	12.5	10.44	41.67	34.8	23.54
450	14	13.87	9.66	46.24	32.2	21.57
475	15	15.56	9.43	51.87	31.43	16.7
525	16	16.43	8.32	54.77	27.74	17.5
550	18	17.58	8.15	58.6	27.17	14.24
575	16	16.12	8.01	53.74	26.7	19.57
600	15	15.83	7.49	52.77	24.97	22.27

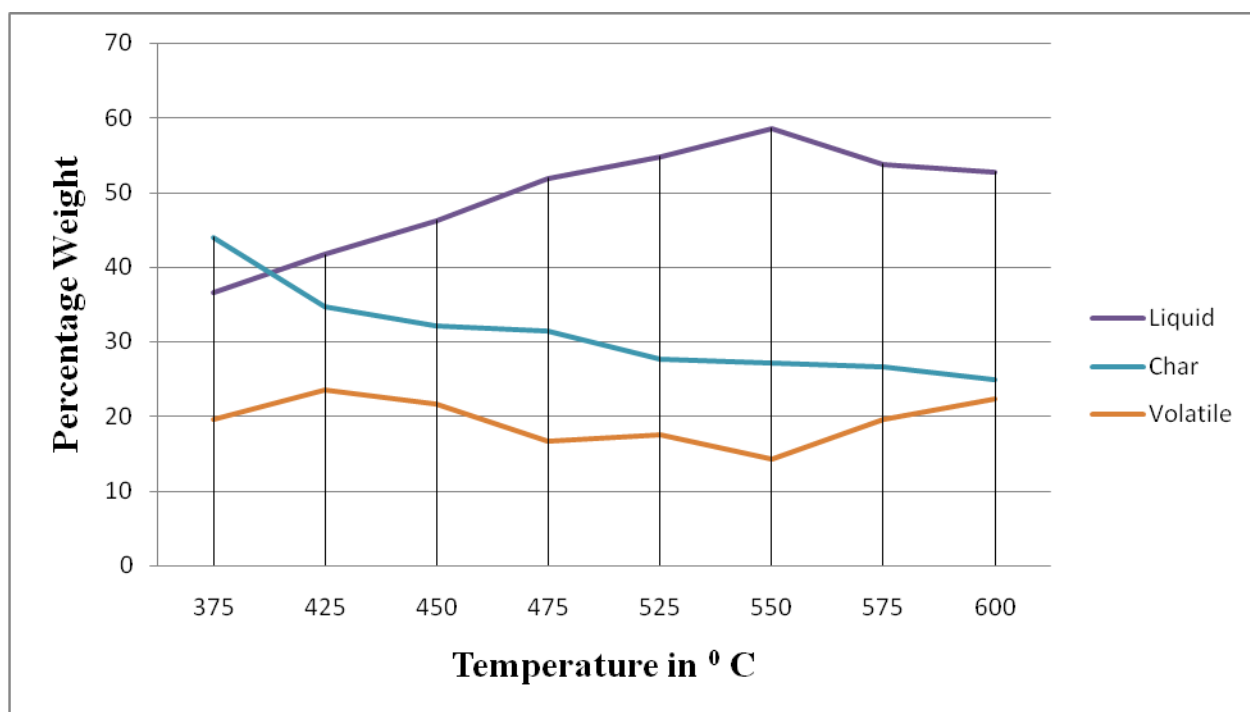


Fig. 4.2 *Product yield with variation of temperature*

4.3 CHARACTERIZATION OF LIQUID PRODUCT

4.3.1 PHYSICAL CHARACTERIZATION

Table 4.4 Physical properties of the obtained liquid product

Property	Value
Maximum Yield	58.6% by weight
Temperature of Maximum yield	550 °C
Appearance	Dark brown free flowing liquid
Odour	Pungent smelling
Density at 15 ⁰ C (gm/cc)	0.9431
Sp. Gravity at 15 ⁰ C/15 ⁰ C	0.9433
Kinematic Viscosity at 40 ⁰ C in Cst	62.05
Pour point in °C	9
Flash Point by Abel method in °C	42
Fire Point by Abel method in °C	46
Gross Calorific Value in Kcal/kg	6709
Sulphur content	1.88 %
Miscibility	Methanol, Ethanol

Table 4.4 enlists various physical properties of the obtained liquid product. It can be seen that the Gross calorific value of the obtained product is 6709 kcal/kg, while that of conventional diesel is nearly 10,200 kcal/kg. The liquid product obtained is lighter than water as is evident from the density value.

It has been found out that methanol and ethanol can be used as a solvent for the liquid product. Sulphur content is an indication of the pollution hazard caused by the combustion of this liquid. As can be seen from the table, the sulphur content is way higher than conventional diesel and for environment friendly operation, additional methods must be employed to reduce or remove the sulphur content.

4.3.2 CHEMICAL CHARACTERIZATION

4.3.2.a GC-MS

The GC-MS of the liquid product produced results which have been shown in table 4.5

Table 4.5 GC-MS of the liquid product

Name of Compound	Area %
Phenol	0.78
p-Cresol	1.41
Phenol, 2-methoxy- Mequinol	0.65
Phenylhydrazine, 3-isopropoxy-2- Trichloromethyl-1-bicyclo[2.2.1] heptane Furan, tetrahydro-2,5-dipropyl-	0.89
1-Dodecene Cyclododecane	1.09
Dodecane	0.40
1-Tridecene	0.36
Indole Indolizine	0.94
Tridecane	0.90
2,4-Imidazolidinedione, 5-ethyl-5-methyl- 26-Methyl-heptacosanoic acid, pyrrolidide Phosphonofluoridic acid, ethyl-, decyl ester	0.52
1-Tetradecene	1.40
Tetradecane	0.89
Ethanone, 1-[1-(4-amino-1,2,5-oxadiazol-3-yl)-5- methyl-1H-1,2,3-triazol-4-yl]-2-morpholino-5 Isopropyl-2,4-imidazolidinedione 5-(4 Chlorobutyl)hydantoin	0.93
1-Pentadecene	0.95
Pentadecane Hexadecane	3.34
N-(Cyclohexyl)succinimide 1-[2-(2- Morpholinoethoxy)ethoxy]-2-(2-hydroxy-1- phenylethoxy)ethane	1.19
Ethyl 2,3-dimethyl-1,3-oxazolidine -2-acetate CeteneZ-8-Hexadecene Cyclotetradecane	0.53
Hexadecane	0.82
8-Heptadecene	1.11
Heptadecane	0.95
Pentadecanenitrile	6.67

Name of Compound	Area %
Pentadecanoic acid, 14-methyl-, methyl ester	1.07
Hexadecanoic acid, methyl ester Hexadecanoic n-Hexadecanoic acid	24.57
9-Eicosyne 5-Eicosyne 7-Heptadecyne	1.24
Oleanitrile 7,14-Methano-4H,6H-dipyrido[1,2- 1',2'-e][1,5]diazocin-4-one, dodec ahydro-, [7S-(7.alpha.,7a.alpha.,1 4.alpha.,14a.alpha.)]- 2,5-Cyclohexadiene-1,4-dione	4.51
9-Octadecenoic acid, methyl ester, (E)- 11-Octadecenoic acid, methyl ester 9- Octadecenoic acid (Z)-, methyl ester Octadecanenitrile Heptadecanenitrile	0.54
9,12-Octadecadienoic acid (Z,Z)- 9,12- Octadecadienoic acid (Z,Z)-Ethyl 9,12- hexadecadienoate	1.85
Oleic Acid 9-Octadecenoic acid,	2.80
Oleic Acid	6.99
Octadecanoic acid	6.49
Hexadecanamide	6.68
N-Methyldodecanamide Decanal, O- methyloxime 2-Hexanone oxime	8.53
9-Octadecenamide	1.73
Octadecanamide	1.34
	0.84

As can be seen from the results of GC-MS Analysis, the main constituent of the liquid product is n-Hexadecanoic acid. The area % for this constituent was found to be maximum.

After this Hexadecanamide is the next major constituent

4.3.2.b FTIR ANALYSIS

The infra-red spectra of the liquid product obtained using FTIR has been shown in figure. The frequencies obtained from the spectra have been compared against reference charts and the interpretation of the results have been shown in table 4.6. As can be seen from the table, carboxylic acids are present in the liquid product. This is also confirmed by the results of GC-MS analysis.

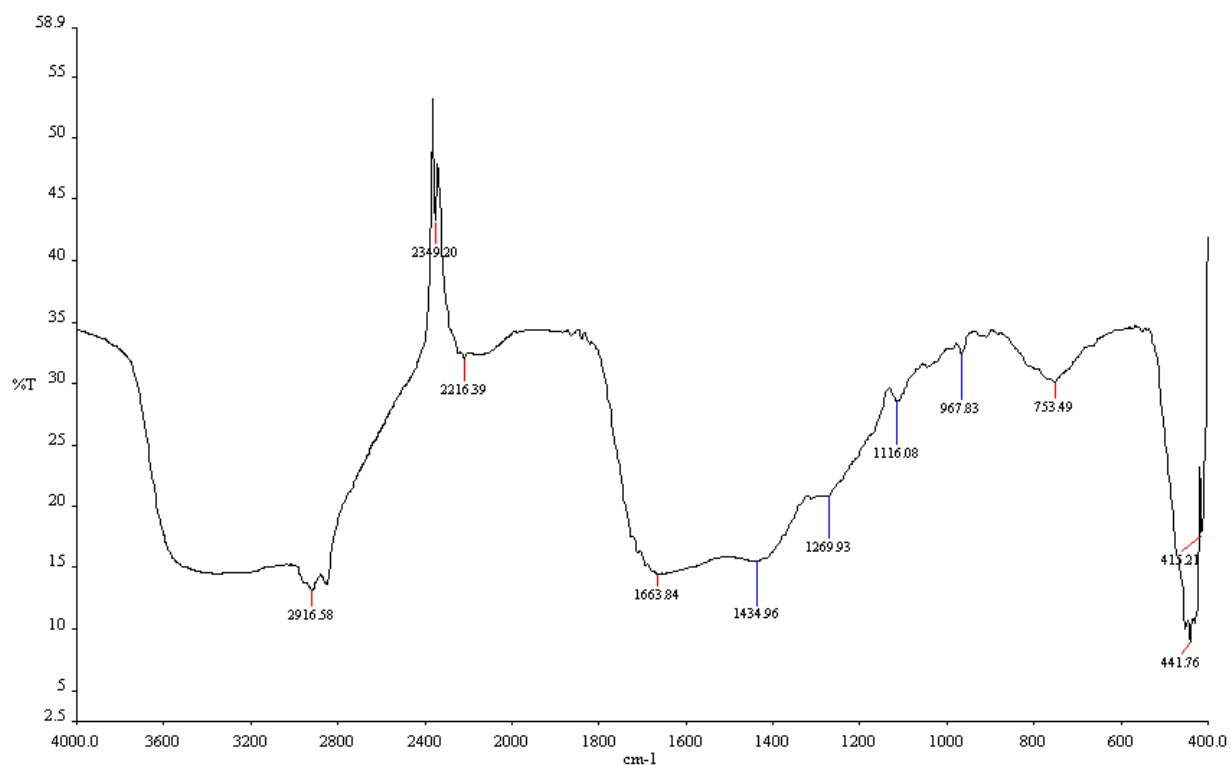


Fig. 4.3 IR Spectra of the liquid product

Table 4.6 FTIR compound and frequency table

Compound Type	Frequency (cm ⁻¹)
C-H Stretch Alkanes	2916.58
C≡C stretch Alkyne	2349.20
C≡C stretch Alkyne	2216.39
C=C stretch alkene	1663.84
C=C stretch aromatic	1434.96
C-O stretch alcohol, ether, ester, carboxylic acid	1269.93
C-O stretch alcohol, ether, ester, carboxylic acid	1116.08
C-H out-of-plane bend Aromatic	967.83

C-H out-of-plane bend Aromatic	753.49
C-X Stretch Bromide Iodide	415.20
C-X Stretch Bromide Iodide	441.76

4.3.2.c ULTIMATE ANALYSIS OF LIQUID PRODUCT

The results of the ultimate analysis of the liquid product have been shown in table 4.7

Table 4.7 Ultimate Analysis of Liquid Product

Ultimate Analysis of Liquid product		
	% N	3.47
	% C	61.47
	% H	4.01
	% S	1.88
	% O	29.17

Chapter 5

CONCLUSION

5 CONCLUSION

Pyrolysis experiments carried out on cotton seed produced a liquid product along with non-condensable vapours and char. The yield of liquid product was maximum at a temperature of about 550⁰C. At this temperature, the yield of liquid product was found to be as high as 58.6% by weight.

Chemical characterization of the liquid product, showed the presence of a large number of organic compounds which included hydrocarbons, organic acids, ketone, phenol, etc. The major constituent as suggested by GC-MS analysis was found to be n-haxadecanoic acid. This is a useful chemical and is used in the manufacture of soap, cosmetics and release agents. Apart from this, it also contains minor amount of alkanes(>C₁₀). These compounds may be recovered by suitable technique and put to commercial use. The calorific value of the liquid product is nearly 60% of that of diesel. High value of pour point suggests loss of fluidity at about 9⁰ C, hence the liquid may not suitable for use as a fuels during winter season.

References

1. Basak B. Uzun and FundaAtes, “Rapid and slow pyrolysis of pistachio shell: Effect of pyrolysis conditions on the product yields and characterization of the liquid product”, *International Journal of Energy Research*, Int. 2007; 31:506–514
2. Singh R.K., Shadangi K.P. Liquid fuel from castor seeds by pyrolysis. *Fuel*. 2011.
3. Singh R.K., Agarwalla A. Kumar S. Pyrolysis of groundnut de-oiled cake and characterization of liquid product. *Bioresource Technology*. 2011
4. Singh R.K., Volli V. Production of bio-oil and de-oiled cakes by thermal pyrolysis. *Fuel*. 2012
5. Singh R.K., Nayan N.K., Kumar S. Production of liquid fuel by thermal pyrolysis of neem seed. *Fuel*. 2012
6. Beis H, Onay O, Koçkar OM. Fixed-bed pyrolysis of safflower seed: influence of pyrolysis parameters on product yields and compositions. *Renew Energy*. 2002;26(1):21–32.
7. Onay O., Mete K. O. Pyrolysis of rapeseed in a free fall reactor for production of bio-oil. *Fuel*. 2006;85:1921–8.
8. Putun E., Uzun B. B., Putun A. E. Fixed-bed catalytic pyrolysis of cotton-seed cake: effects of pyrolysis temperature, natural zeolite content and sweeping gas flow rate. *Bioresource Technology*. 2006;97(5):701–10.
9. Putun A. E., Ozbay N., Varol E. A., Uzun B. B., Ates F. Rapid and slow pyrolysis of pistachio shell: effect of pyrolysis conditions on the product yields and characterization of the liquid product. *International Journal of Energy Resource*. 2007;31:506–14.
10. Mohamad A. S., Chow M. C., Kartini A. B. N. Bio-oils from pyrolysis of oil palm empty fruit bunches. *American Journal of Applied Science*. 2009;6(5):869–75.
11. Ayan E.A., Demiral I. Pyrolysis of grape bagasse: Effect of pyrolysis conditions on the product yields and characterization of the liquid product. *Bioresource Technology*. 2011; 102:3946-3951.
12. Zhongyang L., Shurong W., Yanfen L., Jinsong Z., Yueling G., Kefa C. Research on biomass fast pyrolysis for liquid fuel. *Biomass Bioenergy*. 2004;26:455–62.

13. Sensoz s. “Pyrolysis of safflower (*Charthamustinctorius* L.)Seed press cake: part 1 The effects of pyrolysis parameters on the product yields”,*Bioresour Technol.* 2008 Sep; 99(13):5492-7. Epub 2008 Feb 20.
14. Putun AE, Ozcan A, Gercel HF, Putun E. Production of biocrudes from biomass in a fixedbed tubular reactor. *Fuel* 001;80:1371–8.
15. Beis S.H., Onay O, Kockar OM. Fixed bed pyrolysis of safflower seed: influence of pyrolysis parameters on product yields and compositions. *Renew Energy* 2002;26:21–32.
16. Suat Ucar Ahmet R. Ozkan, “Characterization of products from the pyrolysis of rapeseed oil cake” *Bioresource Technology* 2008; 99: 8771–8776.
17. Filiz Karaosmanogi LU, Esin Culcuogi LU. “Pyrolysis of Rapeseed Cake” *Energy Sources* 2001; 23: 377- 382.